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A NEW READILY PROCESSABLE POLYIMIDE

F. W. Harris and M. W. Beltz
The University of Akron
Akron, OH 44325

P. M. Hergenrother
NASA Langley Research Center
Hampton, VA 23665-5225

Abstract

As part of an effort to develop tough solvent resistance thermoplastics for potential use as structural resins on aerospace vehicles, a new processable polyimide was evaluated. The synthesis involved the reaction of a new diamine, 1,3-bis 2-(3-aminophenoxy)ethyl ether, with 3,3',4,4'-benzophenonetetracarboxylic dianhydride to form the polyamic acid and subsequent conversion of it to the polyimide. Various physical properties such as thermal stability, solvent resistance, glass transition temperature, crystalline melttemperature, melt viscosity and mechanical properties such as fracture toughness, adhesive, film and composite properties are reported. Of particular interest in the extremely high titanium to titanium tensile shear strength obtained for this polyimide.

1. INTRODUCTION

The impetus for research on thermoplastic laminating resins for use in composite structures on aerospace vehicles is lower cost. Thermoplastics offer less waste by virtue of long term stability under ambient conditions, the ability to be reprocessed to correct flaws and the potential of low cost manufacturing. Other properties such as solvent resistance, damage tolerance and long term environmental durability as offered by the new toughened thermosets will also be required of thermoplastics. As part of an effort on thermoplastic laminating resins, several new semi-crystalline polyimides containing ethylenedioxy units have been synthesized.[1-4]

These materials were prepared from the reaction of various aromatic dianhydrides with novel ethylenedioxy containing diamines as shown in Fig. 1. The properties of representative polymers based upon 3,3',4,4'-benzophenonetetracarboxylic dianhydride are presented in Table 1. Based upon a combination of factors such as processability, solvent resistance and availability of monomers, one polymer, the subject of this paper, was selected for more extensive evaluation.

2. EXPERIMENTAL

Monomers - 1,3-Bis 2-(3-aminophenoxy)ethyl ether was prepared by treating the sodium salt of *m*-aminophenol with 2-chloroethyl ether. Recrystallization from ethanol provided white crystals, mp 101-102°C. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) was sublimed at 210°C under vacuum to yield an off-white solid, mp 223-225°C. N-Methylpyrrolidone (NMP) was vacuum distilled over calcium hydride.

Polymer - To a stirred solution of 1,3-bis 2-(3-aminophenoxy)-ethyl ether in NMP under nitrogen, a stoichiometric quantity of BTDA as a powder was added slowly to maintain a well dispersed reaction mixture. The reaction temperature was maintained 25°C by external cooling. After stirring for 2 hours, a viscous pale yellow solution (solids content 20% w/v) formed which was stirred under nitrogen at ambient temperature overnight. The inherent viscosity of the polyamic acid as measured on a 0.5% solution in NMP at 25°C was 0.71 dL/g. The polyamic acid NMP solution was stirred at 200°C for several hours to affect cyclodehydration to the polyimide. Complete cyclodehydration to polyimide yielded a meta-stable solution where the polymer precipitated after standing for several hours. To avoid precipitation, approximately 5-10% of polyamic acid was left in the polyimide (as evidenced by infrared spectroscopic analysis) to yield a relatively stable solution (limited ambient temperature shelf life, longer if refrigerated). For the preparation of moldings, the completely cyclodehyrated polyimide was used. Whereas, polyimide containing 5% of polyamic acid was used to prepare films, adhesive tape and carbon/graphite fabric prepreg. Polymer was isolated by pouring the NMP solution or slurry into water in a blender and subsequently washing well with water and then methanol. The precipitate was collected and dried in vacuo at 200°C for 2 hours to yield an off-white solid.

Characterization - Differential scanning calorimetry (DSC) was performed at a heating rate of 20°C/min. Thermogravimetric analysis (TGA) was conducted at a heating rate of 2.5°C/min in flowing air and nitrogen. Wide angle x-ray scattering (WAXS) data was obtained on powder and film specimens. With the x-ray diffractometer operated at 45 kV and 40 mA using copper radiation with a flat sample holder and a graphite monochromator, the intensity of one second counts taken every 0.01 degrees (2_m) was recorded on hard disk for the angular range: 10-40° (2_m). Melt viscosity was obtained on a Rheometric System IV Rheometer with a parallel plate configuration with the top plate operating in an oscillating mode at different frequencies (0.1 to 100 radians/second). The amplitude was kept small (0.2%) to assure that deformation during the measurement occurred within the linear response range.

Films

Films were prepared by doctoring NMP polymer solutions onto plate glass, stage drying in a circulating air oven to a final temperature of 210°C and holding at 210°C for 2 hours. Mechanical tests were performed according to ASTM D882.

Moldings

In a 1.25 in. square stainless steel mold, polymer powder was compression molded at 250°C under 100 psi. Four compact tension specimens approximately 0.62 in. x 0.62 in. x 0.37 in. thick were cut from the molding and fracture toughness (G_{Ic}, critical strain energy release rate) determined following the procedure in ASTM E399.

Adhesive Specimens

Standard tensile shear specimens (bond area 1 in. wide x 0.5 in. overlap) were fabricated using titanium (Ti, 6Al-4V) adherends having a Pasa Jell 107 (Products Research and Chemical Corp., Semco Div.) surface treatment.

The substrate was primed with a dilute NMP solution (5% solids) of the polyimide and dried for 1 hour at 210°C. Adhesive tapes with (50 phr) and without powdered aluminum MD105 filler were prepared by multiple brush coating of NMP solutions (20 solids) onto 112-E glass with an A-1100 finish. The tape saw a final drying cycle of 210°C in vacuo for 6 hours. Volatile content of the tape was < 0.3%. Specimens were fabricated in a press by heating to 260°C during 45 min. under 100 psi and holding at 260°C under 100 psi for 15 min. Tensile shear specimens were tested according to ASTM D1002.

Composite Specimens

Carbon/graphite fabric (Celion 3KT, BMS 9-8B) was solution coated several times with an NMP solution (15% solids) of the polyimide and subsequently dried after each coat. The resulting prepreg after a final dry at 225°C for 3 hours in air had a resin content of 41% and a volatile content of 1.5%. Eight plies of the prepreg were stacked in a stainless steel mold and press cured for 0.5 hour at 260°C under 200 psi. The composites (3 in. x 7 in. x 0.110 in. thick, resin content of 37%) were cut into specimens and tested for flexural properties and short beam shear strength according to ASTM D790 and D2344 respectively.

3. RESULTS AND DISCUSSION

High molecular weight polyamic acid was readily prepared in NMP from the reaction of 1,3-bis 2-(3-aminophenoxy)ethyl ether and BTDA as represented in Fig. 2. Cyclodehydration to polyimide was affected chemically (acetic anhydride and pyridine) and thermally (heating the NMP solution to 200°C for several hours or by drying a film at 210°C). The resulting polyimide was semi-crystalline as indicated by WAXS (Fig. 3) and DSC (Fig. 4). The polyimide has a crystalline melt temperature (T_m) of 242°C and a glass transition temperature (T_g) of 150°C (Fig. 4). After the T_m has been exceeded, thermal annealing for several hours at 210°C was unsuccessful in inducing crystallinity. Thermogravimetric analysis curves (Fig. 5) showed 5% weight loss in air and in nitrogen at 373 and 408°C respectively. The melt viscosity of fully imidized amorphous polyimide measured at 210°C was 6 x 10^6 poise at a frequency of 0.1 radians/sec and 1 x 10^5 poise at a frequency of 100 radians/sec. The melt viscosity curves of the polyimide, UDEL® P-1700 polysulfone and Ultem® 1000 polyetherimide are shown in Fig. 6.

Our work primarily involved the polyimide prepared by thermal cyclodehydration of the polyamic acid in NMP. When essentially 100% imidization was attained, NMP solutions (10 to 20% solids content) of the resulting polyimide were meta-stable, forming a thick slurry (precipitate of gel-like consistency) upon standing. With heat, the slurry formed a clear solution which upon cooling and standing again became a slurry. When 5-10% of polyamic acid was left in the polyimide, the solution was moderately stable. This solution remained stable for weeks when cold whereas at ambient temperature, the solution formed a thin slurry after several days. This slurry could be transformed back to a solution upon heating and again the solution was stable at ambient temperature for several days (dependent upon the extent of imidization).

Transparent yellow films cast from NMP solutions of 95% imidized polymer and subsequently dried at 210°C gave tensile strength, tensile modulus, and elongation respectively at 25°C of 12,500 psi, 391,400 psi and 4.0% and at 93°C of 9,500 psi, 291,000 psi and 5.0%. Film specimens (0.125 in. x 1.0 in. x 0.002 in. thick) were bent back upon themselves and placed in this stressed condition in jet fuel, deicing fluid, and hydraulic fluid. After 24 hours of immersion, no detectable sensitivity was observed. However after only a few minutes of exposure in methylene chloride (paint stripper component), pronounced crazing was observed.

Transparent orange moldings were fabricated at 260°C under 100 psi and cut into compact tension specimens. Fracture toughness (K_{Ic}, critical stress intensity factor) at 25°C was 2670 psi $\sqrt{}$in and fracture energy (G_{Ic}, critical strain energy release rate) at 25°C was 18.2 in. lb./in.^{2} The surface of the failed specimens was highly crazed and moderately rough due to yielding. For comparison, the G_{Ic} of UDEL® P-1700 polysulfone was 19 in. lb./in.^{2} and of Ultem® 1000 polyetherimide was 21 in. lb./in.^{2}

Standard Ti/Ti tensile shear specimens were fabricated at 260°C under 100 psi and tested to provide the preliminary adhesive data in Table 2. The 25°C average Ti/Ti tensile shear strength of 7850 psi was exceptionally high, perhaps the highest value ever reported for single lap specimens. The failure mode was essentially 100% cohesive. Strengths at other conditions were also excellent with the exception of 72 hour water boil. The problem however was at the interface (adhesive failure) and not with the polyimide. Powdered aluminum filler reduced the 25°C strength somewhat and improved the 121°C strength slightly.

Small graphite fabric composites fabricated at 260°C under 200 psi gave 25°C flexural strength, flexural modulus and short beam shear strength of 70,500, 7,300,000, and 4100 psi respectively. No testing was done at elevated temperature due to the low numbers obtained at 25°C. The exact cause of the low numbers is not known since the graphite appeared to be wetted well, resin content was acceptable, and the overall quality of the composite appeared good. The composite properties were expected to be good based upon the adhesive properties. Other composites will be fabricated from prepreg coated with polyamic acid solution and subsequently dried under conditions to cause imidization.

4. CONCLUSIONS

A new polyimide was synthesized which exhibited resistance to hydraulic fluid, excellent processability, and extraordinary adhesive strength.

5. REFERENCES

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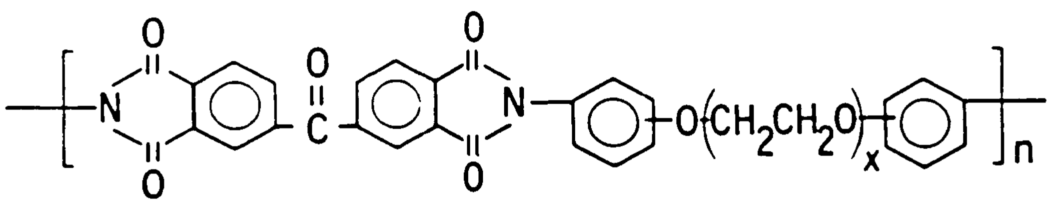
6. BIOGRAPHIES

Frank W. Harris, Professor of Polymer Science at the University of Akron, received a B.S. degree from the University of Missouri and M.S. degree and Ph.D. from the University of Iowa. Dr. Harris was Professor at Wright State University from 1970 to 1983 and became associated with the University of Akron in 1983. His work has been primarily in the area of controlled release of bioactive materials and high performance functional and structural polymers.

Mark W. Beltz, graduate student working towards his Ph.D. at the University of Akron under Dr. Frank W. Harris, received his B.S. degree from Wilmington College and M.S. degree from Wright State University. His work has been primarily in high performance polymers where he has coauthored several papers.

Paul M. Hergenrother, Senior Polymer Scientist in the Materials Division, NASA Langley Research Center, received a B.S. degree from Geneva College and took graduate work at the University of Pittsburgh and Carnegie Mellon University. He held various technical and management positions at Mellon Institute, Koppers Co., Whittaker Corp. (R&D Div.) and Boeing Aerospace Co. and was an Adjunct Research Professor with Virginia Polytechnic Institute and State University. His work has been primarily in the area of high performance polymers.

TABLE I ETHYLENEDIOXY POLYIMIDES



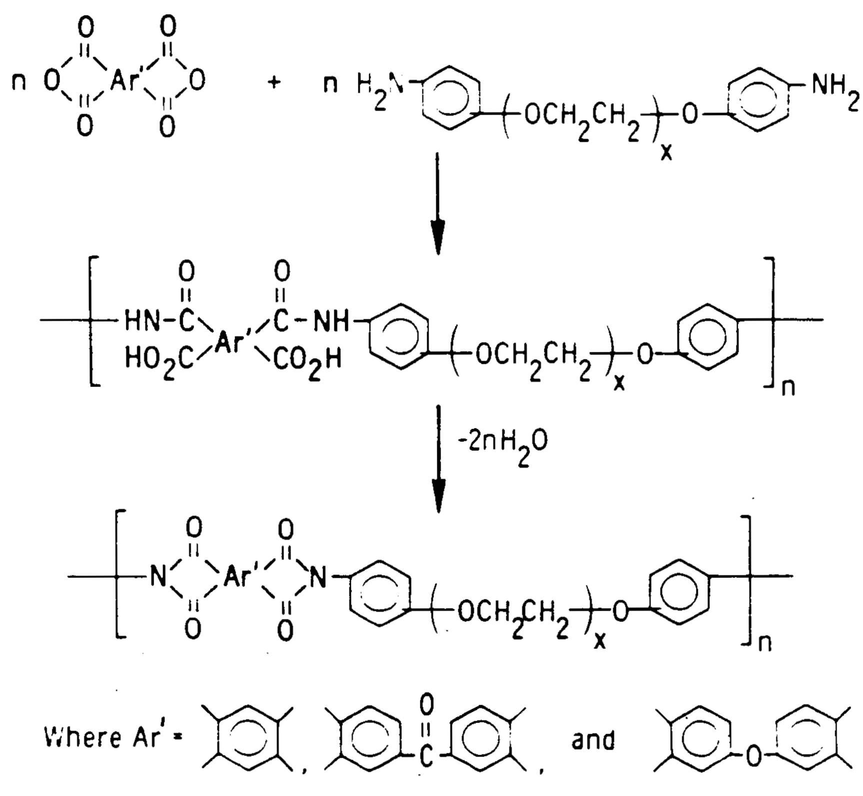
x =	meta, meta		para, para	
	Tg, ^{o}C	Tm, ^{o}C	Tg, ^{o}C	Tm, ^{o}C
1	191	290	246	460
2	155	236	235	410
3	-	-	200	395

TABLE 2 Ti/Ti TENSILE SHEAR STRENGTHS

FILLER	TEST CONDITION	TENSILE SHEAR ST., PSI (FAILURE)[2]
NONE	25°C	7850 (COH)
	25°C AFTER 3 DA H_2O BOIL	3040 (ADH)
	93°C	5400 (COH)
	121°C	4045 (COH + TP)
50 PHR MD105AL	25°C	6200 (COH)
	25°C AFTER 3 DA H_2O BOIL	3610 (ADH)
	93°C	5030 (COH)
	121°C	4300 (COH)

[1] PASA-JELL 107 SURFACE TREATMENT, 25°C • 260°C UNDER 100 PSI, HOLD 15 MIN
[2] COH = COHESIVE, ADH = ADHESIVE, AND TP = THERMOPLASTIC

FIG. 1 SYNTHESIS OF ETHYLENEDIOXY POLYIMIDES



x = 1 to 4

FIG. 2 SYNTHESIS OF ETHYLENEDIOXY POLYIMIDE

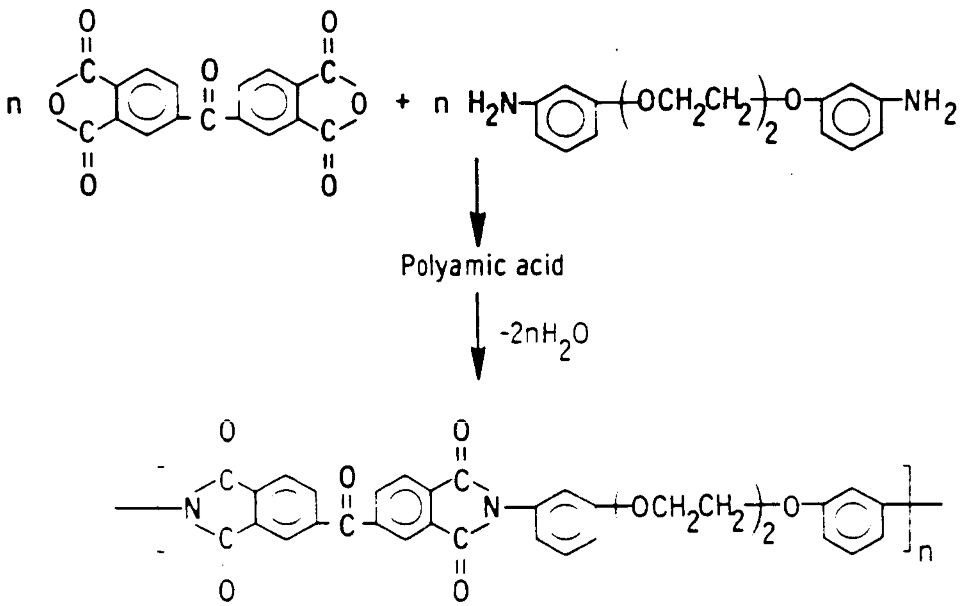


FIG. 3 WIDE ANGLE X-RAY DIFFRACTOGRAMS

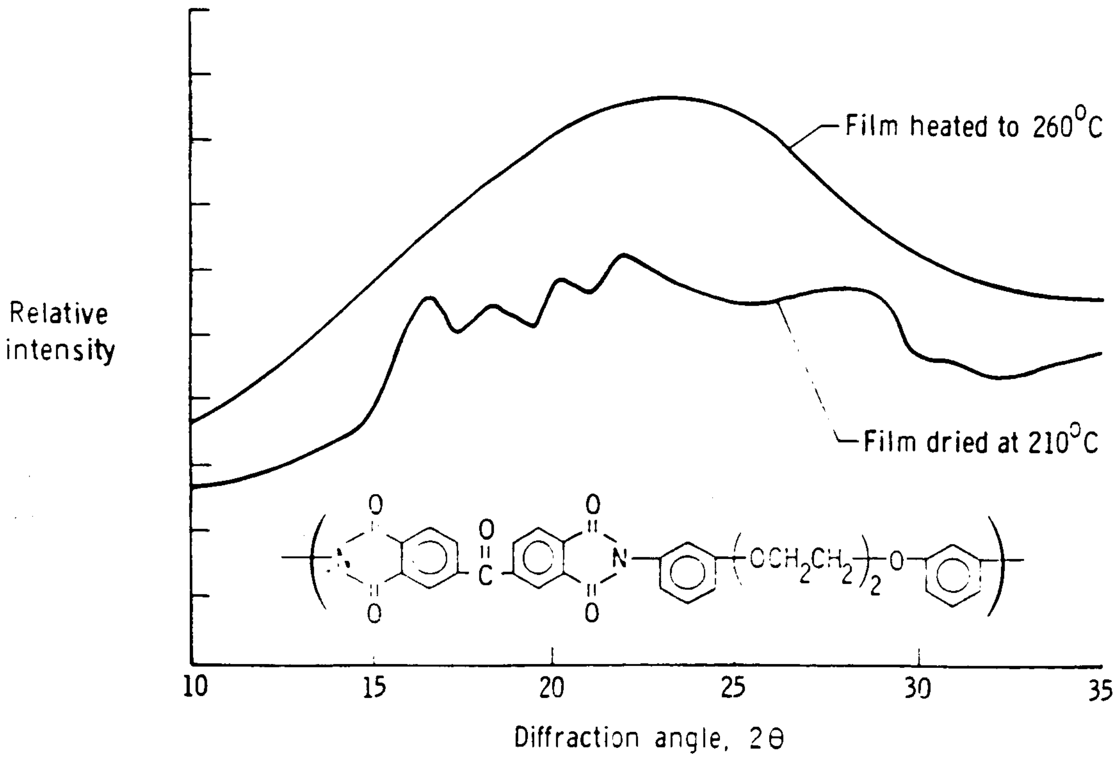


FIG. 4 DIFFERENTIAL SCANNING CALORIMETRIC CURVES

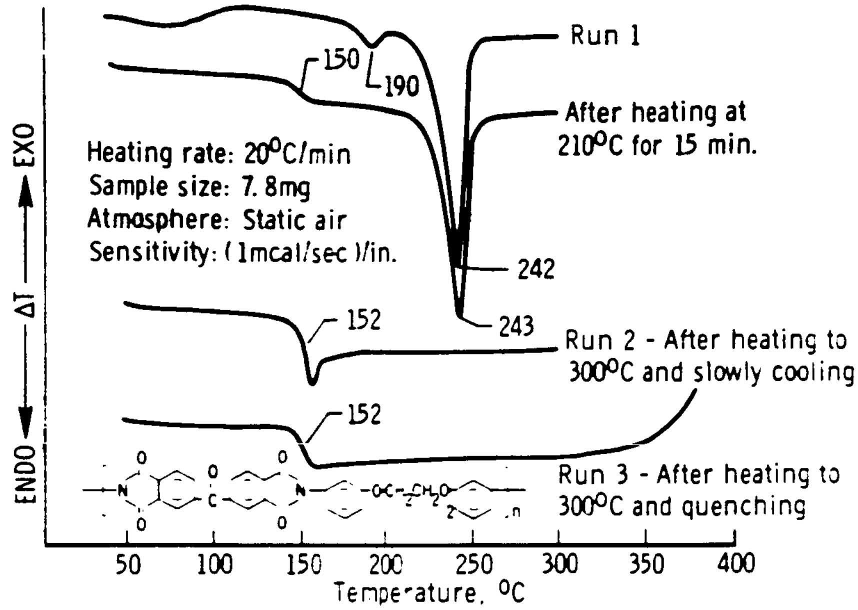


FIG. 5 THERMOGRAVIMETRIC ANALYSIS CURVES

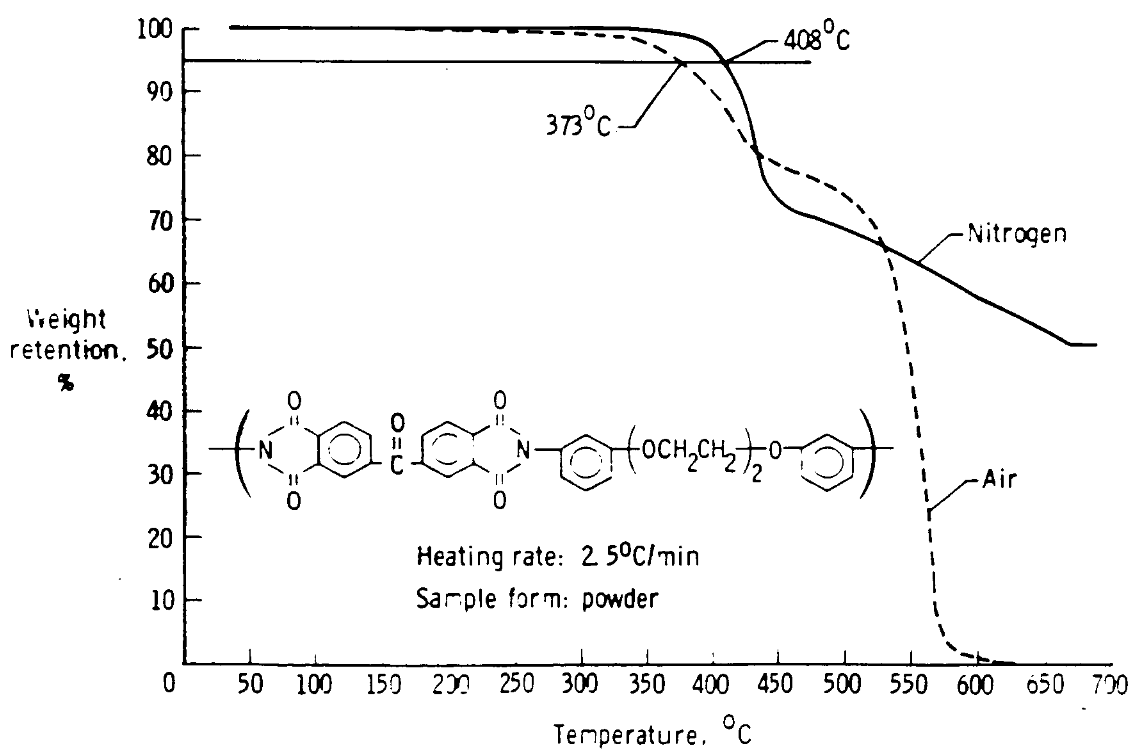


FIG. 6 MELT VISCOSITY OF THERMOPLASTICS